Short communication

Enhancement effect of trace H_2O on the charge–discharge cycling performance of a Li metal anode

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HIGHLIGHTS

- Trace H_2O with CO_2 in the electrolyte enhances the cycling of a Li metal anode.
- The cycling life increases steeply with the increasing the H_2O content up to 35 ppm.
- Enhanced cycling life is observed to be due to the surface products of the SEI.
- Effective SEI layer was produced by way of the reactions related to the trace H_2O.

GRAPHICAL ABSTRACT
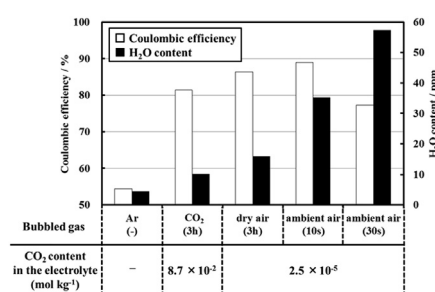
ARTICLE INFO

ABSTRACT

The effects of a small amount of H_2O with and without CO_2 in an electrolyte of 1 M $LiPF_6$/ethylene carbonate and diethyl carbonate on the cycling life of a Li metal anode is investigated in this paper using charge–discharge cycling. A low cycling performance, which is less than 55%, is observed with the electrolyte with trace H_2O but without CO_2; however, when the trace H_2O is accompanied by CO_2, performance drastically improves and coulombic efficiency reaches a maximum of 88.9%. In the presence of CO_2, the cycling performance is found to be strongly affected by the H_2O content in the electrolyte, and increases with an increase in H_2O content of up to 35 ppm. From an X-ray photoelectron spectroscopy analysis, trace H_2O is found to affect the compounds of the solid electrolyte interphase (SEI) on the lithium surface and produces an Li_2CO_3 and LiF layer on the upper part of the SEI, both known to be good passivation layers for preventing side reactions during charge–discharge cycling.

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1. Introduction

Lithium (Li) metal (3860 mAh g^{-1}, 2060 mAh cm^{-3}) shows promise as a negative electrode for use in large-scale energy storage, an increasingly important area owing to the recent emphasis on reducing energy consumption and increasing the use of renewable energy. However, side reactions with the electrolyte solution during charge–discharge cycling and dendritic growth of the Li anode can cause a serious degradation of reversible capacities and the short circuit. The influence of trace H_2O and gas species in ambient air on a lithium metal anode's cycling ability has become an important subject relating to the practical application of the non-aqueous Li–air battery. It has been reported that dissolved CO_2, dry air [1–3], and some additives (vinylene carbonate, fluoroethylene carbonate [4–6], and hydrofluoric acid (HF) [7]) in the electrolyte improve the cycling performance of Li metal anodes and

restrict the dendritic growth. In particular, Li deposited with CO_2 or dry air has been shown to have a protective effect against large amounts of H_2O and some of the reactive contaminations caused by the products formed on the Li surface during the initial deposition.

This study examines the effect of trace H_2O, with and without CO_2, in 1 M $LiPF_6$/ethylene carbonate (EC) and diethyl carbonate (DEC) electrolyte on the charge–discharge cycling lifespan of an Li metal anode, following the procedure proposed by Koch et al. [8]. The enhancement effect of trace H_2O in the presence of CO_2, and the dependence of the cycling performance on the H_2O content in the electrolyte is demonstrated using an electrolyte bubbled with CO_2 gas, dry air, and ambient air.

2. Experimental procedure

Electrochemical characterization was performed in a three-electrode beaker cell. A Ni disk (diameter: 5 mm, purity: 99.99%) was prepared as the working electrode and lithium foils were used for the reference and counter electrode. An electrolyte solution of 1 M $LiPF_6$ (EC : DEC = 50 : 50 volume %), which has a H_2O content of less than 20 ppm was purchased from Kishida Chemical Co., Ltd. The coulombic efficiency of the lithium metal anode was estimated using the charge–discharge cycling test proposed by Koch et al. [8]. Prior to the cycling test, carbon dioxide gas or dry air were bubbled for 3 h in order to saturate the H_2O content in the electrolyte, and ambient air was bubbled for 5, 10, 30, or 60 s.

In this study, 5.1 C cm^{-2} of lithium was initially electrodeposited onto a nickel substrate at 2.0 mA cm^{-2} and then 1.0 C cm^{-2} or 2.4 C cm^{-2} was discharged (dissolved) and charged (deposited) at 2.0 mA cm^{-2} in each subsequent cycle. The end-point of the cycling life was detected by the potential to 1 V vs. Li/Li$^+$. As for the preparation of the electrolyte, carbon dioxide gas (H_2O content < 50 ppm, purity: 99.99%), dry air (H_2O content < 21 ppm), or ambient air (humidity = 51 ± 1%) were separately bubbled into their respective pristine electrolytes before the charge–discharge test. The H_2O content in each test solution was measured using the Karl Fischer method (AQ-7, Kyoto Electronics Manufacturing Co., Ltd) and the CO_2 amount was saturated under the partial pressure of the atmosphere. All of the charge–discharge tests were conducted in an Ar-filled glove box with dew point below −110 °C (<1.6 ppb of H_2O).

The elementary chemical state on the Li surface was revealed using X-ray photoelectron spectroscopy (XPS) (VersaProbe-II, ULVAC-PHI). Monochromatic Al−K radiation (1486.6 eV), operated at a power of 25 W (15 kV), was applied as the X-ray source. Sputtering of the sample surface was performed using an Ar$^+$ ion gun under an accelerating voltage of 3 kV and measurements were made after 0, 2, 4, 6, 8, and 10 min of Ar$^+$ ion sputtering. All of the samples were washed with pure dimethyl carbonate, dried under a vacuum, and then transferred to chambers using a transfer vessel under an Ar atmosphere.

3. Results and discussion

Fig. 1 shows the coulombic efficiency of the lithium metal anode and the H_2O content in each electrolyte solution, obtained from the electrolytes bubbled with carbon dioxide gas (3 h), dry air (3 h), or ambient air (10 s or 30 s), and the electrolyte that underwent no bubbling. The amounts of lithium at initial deposition and during charge–discharge cycling are 5.1 C cm^{-2} and 1.0 C cm^{-2}, respectively. The amount of dissolved CO_2 in the electrolyte mentioned in this figure was estimated by Henry's law constants [9]. The coulombic efficiency of the unbubbled electrolyte, i.e., with trace H_2O but without CO_2, is less than 55%, but the efficiency obtained with trace H_2O in the presence of CO_2 is over
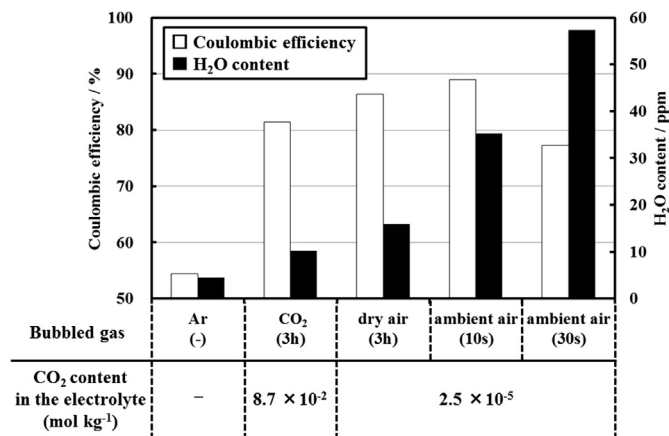

Fig. 1. Effects of H_2O content in the electrolyte bubbled with CO_2 gas (3 h), dry air (3 h), ambient air (10 s and 30 s), and without bubbling on the coulombic efficiency of a lithium metal anode. (The result obtained from the electrolyte without bubbling (i.e., the pristine electrolyte) is described as "Ar (−)" in this figure.).

75%, with a maximum of 88.9%, 34.5% higher than that obtained without CO_2.

Enhanced cycling performance caused by the presence of CO_2 gas is still observed, even when an electrolyte solution of EC mixed with DEC was used in place of the propylene carbonate (PC) solution [1]. As for H_2O content, it was slightly increased in the electrolyte that was bubbled with CO_2 gas. The cycling performance obtained with dry air (3 h) is superior to that obtained with CO_2 gas, even though the amount of CO_2 dissolved in the electrolyte with dry air is theoretically the lesser of the two.

In light of the authors' previous report [3], which asserts that dissolved nitrogen (N_2), oxygen (O_2), and argon (Ar) do not improve Li metal cycling performance, this enhanced cycling performance is considered to be due to the effect of both CO_2 and H_2O in the electrolyte. In fact, the H_2O content in the electrolyte bubbled with dry air (3 h) is higher than that with CO_2 gas (3 h). It is also confirmed that the cyclability obtained from the electrolyte bubbled with dry air (6 h) is approximately the same as that with dry air (3 h), since the H_2O content in these electrolytes is nearly equal. The strong dependence of the cycling performance on the amount of H_2O in the electrolyte is observed from the bubbling conducted with ambient air. The coulombic efficiency with ambient air (10 s) is higher than that with CO_2 gas and with dry air (3 h), whereas it is lower with ambient air (30 s).

This result indicates that an optimum H_2O amount exists for achieving the longest cycling life of a lithium metal anode. The reason ambient air (10 s) results in a higher cycling performance than dry air (3 h) is thought to be due to the presence of H_2O in the electrolyte, since the amount of dissolved CO_2 in these solutions is equal. From the results described above, it is concluded that trace H_2O in the presence of CO_2 in the electrolyte plays a significant role in determining the cycling performance of a Li metal anode, and that it also contributes to an increase in cycling performance by a certain amount, regardless of the bubbled gas species, i.e., carbon dioxide gas, dry air, or ambient air.

Fig. 2 shows the coulombic efficiency obtained when the amount of lithium deposited/dissolved during charge–discharge cycling was varied. The amount of lithium during cycling was set to 1.0 C cm^{-2} and 2.4 C cm^{-2} for the right- and left-hand conditions, respectively, with the loading current at 2.0 mA cm^{-2}. The coulombic efficiency is observed to change depending on the coulombic amount of lithium during cycling, and it tends to decrease with an increase in the amount of lithium. Increasing the
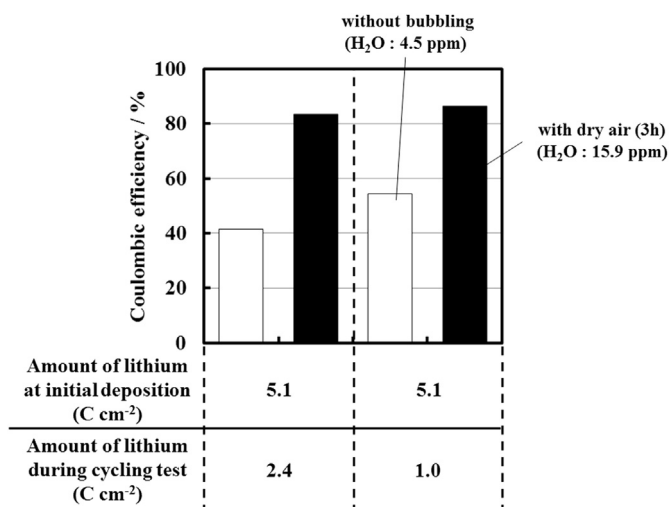
Fig. 2. Coulombic efficiency of a lithium metal anode under different charge–discharge conditions (a black or white bar shows the result obtained from the electrolyte with or without dry air bubbling, respectively).

amount of lithium during cycling suggests a more intense condition, that is to say, a larger amount of active lithium is exhausted for dissolution. However, for each condition, the cycling performance using dry air (3 h) is superior to that without bubbling, and remained over 30% higher. This confirms the predominant effect of trace H_2O in the presence of CO_2 on cycling performance, even when the charge–discharge condition is changed.

To understand the effect of H_2O on cycling performance in detail, the charge–discharge test was conducted under several different conditions, by changing the bubbling time (5, 10, 30, and 60 s) in order to vary the H_2O content in the electrolyte; ambient air was used throughout. The results for coulombic efficiency as a function of H_2O content in the electrolyte are shown in Fig. 3. The H_2O content in the electrolyte increases with an increase in bubbling time: the coulombic efficiency increases steeply with an increase of H_2O content until approximately 35 ppm, reaching a maximum coulombic efficiency of 88.9%, before decreasing gradually as H_2O content continues to increase. This remarkable enhancement affected by trace H_2O below 35 ppm is similar to the trend observed in Fig. 1. This strongly suggests that trace H_2O in the electrolyte affects the cycling performance of the lithium metal anode.
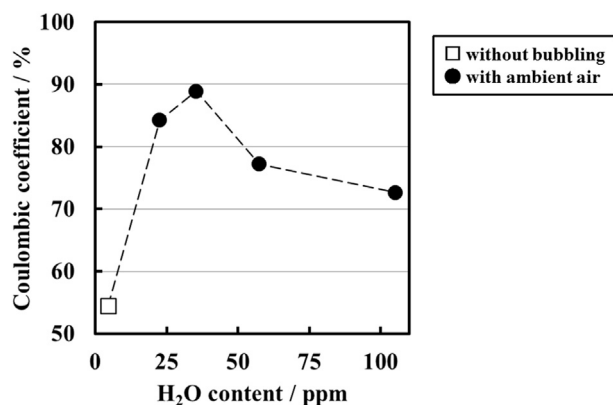

Fig. 3. Effects of H_2O content in the electrolyte bubbled with ambient air for 0, 5, 10, 30, and 60 s on the coulombic efficiency of a lithium metal anode.

According to the authors' previous reports [2,3], both dissolved CO_2 in the electrolyte and the charge–discharge atmosphere affect the SEI layer, which is formed on the deposited lithium surface and whose characteristics were found to strongly affect the cycling performance of the lithium metal anode. In other words, investigation of the SEI layer is important in order to account for the enhancement effect on cycle performance. In order to clarify the effect of trace H_2O on the SEI's chemical structure, XPS analysis was performed after an initial deposition of lithium of 5.1 C cm^{-2}.

Fig. 4 illustrates the O 1s spectra of the SEI obtained from the lithium in the electrolyte with and without ambient air bubbling for 10 s. Ar$^+$ etching was used to obtain information about the inner part of the SEI's compounds. For the O 1s spectra without bubbling, the peak of the surface SEI is around 533.5 eV, which is attributed to lithium alkyl carbonates (ROCO$_2$Li) [10]. After Ar$^+$ etching, the main peaks of the O 1s shifted to a lower binding energy, with peak energy close to 531.5 eV; these are assumed to be Li_2CO_3 [11], with a shoulder around 532.5–533.5 eV.

It is also suggested that the inner part of the SEI obtained from the lithium in the electrolyte that did not undergo bubbling is composed of Li_2CO_3 as well as ROCO$_2$Li. The amount of ROCO$_2$Li in the inner part of the SEI is observed to be smaller than that of Li_2CO_3. This result is in agreement with those reported by our previous study [2,3] and Kanamura et al. [7]. It's well-known that a part of the SEI composed of ROCO$_2$Li is a main channel for lithium ions since the diffusion coefficient of lithium ions in the organic lithium compounds is reported to be higher than that in the inorganic lithium compounds [12]. Therefore we consider that lithium alkyl carbonate in SEI, whose composition ratio is relatively small, still works as a pathway for Li ion's penetration during charge–discharge cycling. On the other hand, the main surface peaks of O 1s in the spectra obtained from the lithium in the electrolyte with ambient air (10 s) are around 531.5 eV; in other words, Li_2CO_3 is the main compound on the surface of the SEI. The inner part of the SEI with ambient air (10 s) showed similar properties to those without bubbling, except for the appearance of the peak, which is located at around 528.0–529.0 eV after Ar$^+$ etching for 2 to 4 min. This peak is attributed to Li_2O [6] and this compound is thought to be produced by the reaction between H_2O and Li$^+$ [13].

As a result, a significant difference between the SEI formed with ambient air and that formed without ambient air is observed on the surface layer; specifically, the main product of the former is Li_2CO_3, but of the latter is ROCO$_2$Li. The Li 1s spectra also showed a similar difference in chemical structure as that of the SEI shown in O 1s. In the electrolytes where ambient air was used, this was considered to be due to a reaction between an lithium alkyl carbonate (ROCO$_2$Li), which formed on the SEI surface, and trace H_2O in the electrolyte, resulting in Li_2CO_3 as per the reaction below [11,14,15]:

$$2ROCO_2Li + H_2O \rightarrow Li_2CO_3 + 2ROH + CO_2 \qquad (1)$$

Fig. 5 illustrates the surface composition ratio of SEI as a function of H_2O content in the electrolyte bubbled with CO_2 gas (3 h), dry air (3 h), ambient air (10 s and 60 s), and without bubbling. Each composition ratio was estimated by the peak resolution of the O 1s spectra with respect to Li_2CO_3 (531.5 eV), ROCO$_2$Li (533.0 eV), and Li_2O (528.0 eV). Regardless of the bubbled gaseous species, the Li_2CO_3 ratio was found to increase with an increase of H_2O content in the electrolyte, whereas the ROCO$_2$Li ratio decreases. This indicates that Li_2CO_3 forms on the surface of the SEI, caused by trace H_2O in the electrolyte.

Generally, Li_2CO_3 is regarded as a good passivation agent that can protect the lithium metal anode from side reactions with the electrolyte during charge–discharge cycling [2,16]. It has even been
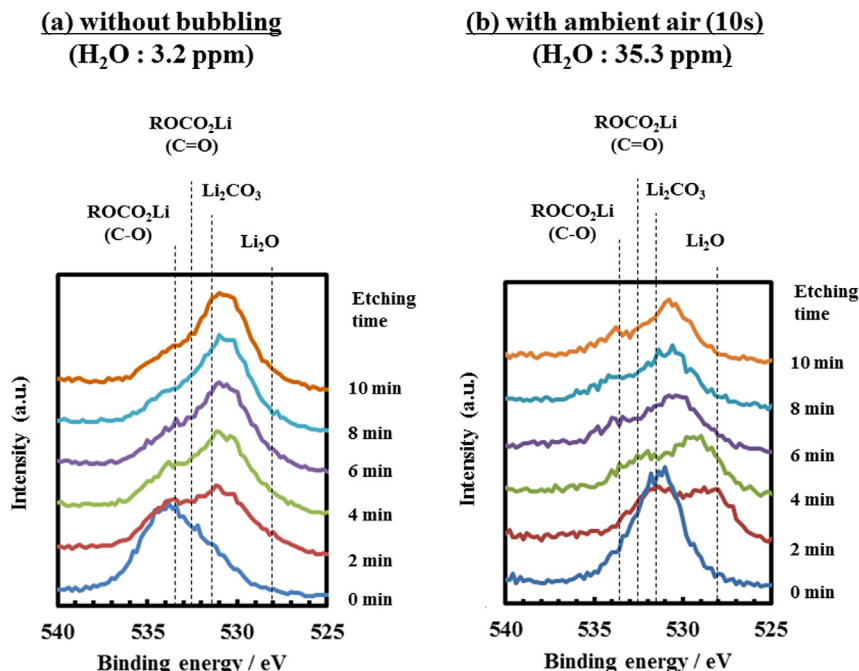
(a) without bubbling
(H_2O : 3.2 ppm)

(b) with ambient air (10s)
(H_2O : 35.3 ppm)

Fig. 4. XPS spectra of O 1s for an electrodeposited lithium anode obtained from the electrolyte (a) without bubbling and (b) with ambient air (10 s).
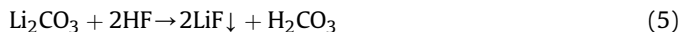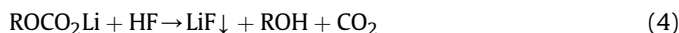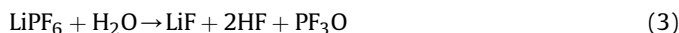
reported that dissolved CO_2 in the electrolyte also contributes to the production of Li_2CO_3 in the SEI layer and the enhancement of cycling performance [1,17]. Therefore, trace H_2O with CO_2 is considered to achieve a still greater enhancement of cycling performance, owing to the formation of Li_2CO_3.

As Fig. 3 shows, the coulombic efficiency decreases with a further increase in H_2O content over 35 ppm. In order to understand this phenomenon, an XPS analysis was carried out to investigate the SEI generated by the electrolyte with ambient air (10 s and 60 s). Fig. 6 shows the F 1s spectra of the initially deposited lithium of 5.1 C cm^{-2}. In these surface spectra, the F 1s peak appears at 685.0 eV, which corresponds to LiF [10]. In contrast, the spectra obtained from the inner part of these SEI layers reveals quite different features. The peak binding energy of the lithium deposited from the electrolyte with ambient air (10 s) appears to shift to a higher binding energy (687.0 eV), which is attributed to $Li_xPF_yO_z$ [10]. On the other hand, the peak binding energy of the lithium deposited from the electrolyte with ambient air (60 s) remains constant, *i.e.*, a thick layer of LiF is formed in the presence of a larger amount of H_2O in the electrolyte. It is well-known that LiF is

produced on the surface of the SEI, and is caused by the disproportionation reaction of $LiPF_6$ [18]:

$$PF_6^- + 3Li^+ + 2e^- \rightarrow 3LiF\downarrow + PF_3 \qquad (2)$$
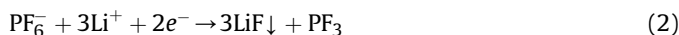
In addition, a thick layer of LiF under a large amount of H_2O in the electrolyte is thought to be formed as a result of the reaction between the compounds of the SEI, such as $ROCO_2Li$, Li_2CO_3, and Li_2O, and hydrogen fluoride (HF), which is produced as a result of the reaction between H_2O and $LiPF_6$, as described below [7,14]:

$$LiPF_6 + H_2O \rightarrow LiF + 2HF + PF_3O \qquad (3)$$

$$ROCO_2Li + HF \rightarrow LiF\downarrow + ROH + CO_2 \qquad (4)$$

$$Li_2CO_3 + 2HF \rightarrow 2LiF\downarrow + H_2CO_3 \qquad (5)$$

$$Li_2O + 2HF \rightarrow 2LiF\downarrow + H_2O \qquad (6)$$

It has been reported that LiF also has a protective function with regard to the lithium metal anode from the electrolyte. In particular, a thin LiF layer is believed to contribute to an increase in the coulombic efficiency of the lithium metal anode during charge–discharge cycling, owing to the restriction of the side reaction on the surface of the lithium metal; however, the ionic conductivity of LiF is much smaller than that of Li_2CO_3 or the other compounds in the SEI [19]. In fact, the overpotential during lithium deposition obtained from the electrolyte with ambient air at 60 s was observed to be slightly higher (by 15 mV) than that with ambient air at 10 s, since thicker LiF forms on the SEI layer with ambient air at 60 s. This increased overpotential may lead to a promotion of side reactions of the electrolyte and result in a deterioration of the cycling performance in the presence of a large amount of H_2O.

From the discussions above, the thickness of each compound in the SEI layer, as well as its composition, are also considered to be important properties for the restriction of side reactions since they relate to the ionic conductivity of lithium ions and overpotential during charge–discharge cycling. SEI's composition and its
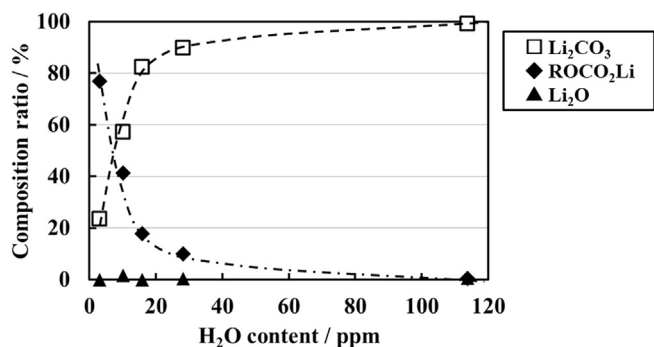

Fig. 5. Dependence of the composition ratio of the SEI surface estimated by O 1s spectra on the H_2O content in the electrolyte.

(a) with ambient air (10s)
(H_2O : 35.3 ppm)

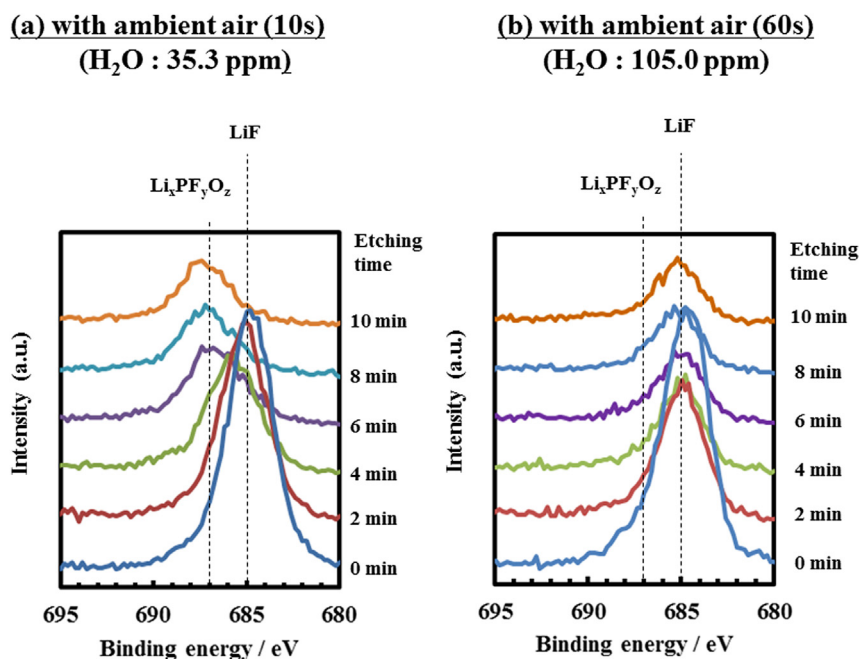## (b) with ambient air (60s)
(H_2O : 105.0 ppm)

Fig. 6. XPS spectra of F 1s for an electrodeposited lithium anode obtained from the electrolyte with ambient air for (a) 10 s and (b) 60 s.

thickness should be controlled in order to achieve a longer cycling life of lithium metal anode.

4. Conclusion

The enhancement effect of trace H_2O in a $LiPF_6$/ethylene carbonate and diethyl carbonate electrolyte in the presence of saturated CO_2 on the charge–discharge cycling performance of Li metal anodes has been confirmed. The cycling performance was found to be strongly affected by the H_2O content in the electrolyte and reached a maximum increase of 34.5% as compared to a pristine electrolyte. This enhanced performance appeared to be caused by the SEI's surface products, such as Li_2CO_3 and LiF, which resulted from reactions related to the presence of trace H_2O in the electrolyte.

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